

## PATENT ABSTRACTS OF JAPAN

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## (54) METHOD FOR PRODUCING POLYAMIDE RESIN

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing a polyamide resin whose gelation is suppressed.

SOLUTION: This method for producing the polyamide resin in which  $\geq 70$  mol. % of a diamine component is m-xylenediamine and further in which the total contents of tertiary nitrogen comprising nitrogen based on imino compounds and nitrogen based on tertiary amides is  $\leq 0.5$  mol. % with respect to the total nitrogen content based on secondary amides, comprising a continuous process consisting mainly of a raw material-preparing process, an salt-formation process, an pre-polymerization process and a post-polymerization process, controls supply accuracy C/A (molar ratio: dicarboxylic acid/diamine) to 1.025 to 0.975, when the dicarboxylic acid and the diamine are supplied from the raw material-preparing process to the salt-formation process, controlling a salt concentration, namely the aqueous concentration of the aminocarboxylic acid salt produced from the amine and the dicarboxylic acid in the amidation process, to  $\geq 80$  wt.%, and further controlling a retention time, namely a time needed from the start of the supply of the raw materials to the salt-formation process to the discharge of the polyamide resin, to  $\leq 210$  min.

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[Scope of Claims]

1. A method for producing a polyamide resin, in which 70% by mol or more of a diamine component is m-xylylene diamine; and

a content of tertiary nitrogen, represented by molar ratio of the sum of nitrogen based on an imino compound and nitrogen based on a tertiary amide relative to nitrogen based on a secondary amide, is 0.5% by mol or less,

being characterized by comprising continuous steps mainly made up of a raw material blending step, an amidation step, an initial polymerization step and a late polymerization step,

wherein a supply accuracy C/A (molar ratio: dicarboxylic acid/diamine acid) at the time of supplying the dicarboxylic acid and the diamine from the raw material blending step to the amidation step is in the range of from 1.025 to 0.975;

a salt concentration, which is a concentration of an aqueous solution of an aminocarboxylic acid salt produced from the diamine and the dicarboxylic acid in the amidation step, is 80% by weight or more; and

a retention period of time, which is a time duration required from the start of the supply of the raw material to the amidation step to discharge of the polyamide resin, is 210 minutes or less.

[0011]

[Mode for Carrying Out the Invention]

In a polyamide resin according to the invention, 70% by mol or more of a diamine component constituting the polyamide is m-xylylene diamine (MXD). When MXD is less than 70% by mol in the diamine component constituting the polyamide, an oxygen barrier property is extremely deteriorated. In the polyamide resin according to the invention, MXD in the diamine component constituting the polyamide is, preferably, 75% by mol or more and, more preferably, 80% by mol or more.

[0012]

The component constituting the polyamide resin according to the invention is not particularly limited so long as MXD in the diamine component is 70% by mol or more; however, as the component constituting the above-described polyamide resin, m-xylylene adipamide (MXD-6) which is obtained from MXD and adipic acid (AA), m-xylylene sebacamide (MXD-10) which is obtained from MXD

and sebacic acid (hereinafter, referred to sometimes as "SA"), and m-xylylene isophthalamide (MXD-I) which is obtained from MXD and isophthalic acid (hereinafter, referred to sometimes as "IPA") are preferred. Further, a copolymerized polyamide to be obtained from MXD and an acid component in which two types or three types selected from among the above-described AA, SA and IPA are combined at given ratios is also preferred.

[0013]

As for diamine components constituting the polyamide resin according to the invention, other diamines than MXD can each be used in the range of less than 30% by mol in the diamine component. Examples of such diamines include aliphatic diamines such as ethylene diamine, 1-methylethylene diamine, 1,3-propylene diamine, tetramethylene diamine, pentamethylene diamine, hexamethylene diamine, heptamethylene diamine, octamethylene diamine, nonamethylene diamine, decamethylene diamine, undecamethylene diamine and dodecamethylene diamine; alicyclic diamines such as cyclohexane diamine, bis-(4,4'-aminohexyl)methane; and aromatic diamines such as p-xylylene diamine. These diamines can be used in combinations of two types or more at given combination ratios. Among the above-described

diamine components, hexamethylene diamine and p-xylylene diamine are preferred.

[0014]

As for acid components constituting the polyamide resin according to the invention, other acids than the above-described AA, SA and IPA can be used. Examples of such acids include aliphatic dicarboxylic acids such as malonic acid, succinic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, undecanoic acid, undecanedioic acid, dodecanedioic acid and a dimer acid; alicyclic dicarboxylic acids such as 1,4-cyclohexane dicarboxylic acid; and aromatic dicarboxylic acids such as terephthalic acid, phthalic acid, xylylene dicarboxylic acid and naphthalene dicarboxylic acid. These dicarboxylic acids can be used in combinations of two types or more at given combination ratios.

[0024]

In the method for producing the polyamide resin according to the invention, constitution of apparatuses for performing each step of a raw material blending step, an amidation step, an initial polymerization step and a late polymerization step which mainly constitute the above-described continuous steps, and actually performing

conditions are not particularly limited so long as they are within the ranges of conditions denoted in the above-described (1) to (4). Hereinafter, each step will be described in detail.

[0025]

The raw material blending step is performed by an apparatus containing a melting/storage tank for each raw material of the dicarboxylic acid and the diamine and a raw material supply pump for sending each of the dicarboxylic acid and diamine to the amidation step. Since the dicarboxylic acid is a solid, it is melt/stored in the melting/storage tank. A melting/storing temperature of the dicarboxylic acid is preferably from a melting point thereof to the melting point plus 20°C. When the melting/storing temperature is allowed to be unduly high, a thermal degradation or thermal decomposition of the dicarboxylic acid occurs, while, when the melting/storing temperature is allowed to be unduly low, an uneven melting occurs, to thereby deteriorate a raw material supply accuracy to the amidation step. Further, a melting/storing temperature of the diamine is preferably from a melting point thereof to the melting point plus 40°C. When the melting/storing temperature is allowed to be unduly high in the same manner as in the dicarboxylic acid, a thermal degradation or thermal decomposition of

the diamine occurs, while, when the melting/storing temperature is allowed to be unduly low, an uneven melting occurs, to thereby deteriorate a raw material supply accuracy to the amidation step. In order to suppress a thermal oxidative decomposition of the dicarboxylic acid and the diamine, it is preferable that they are put in an inert gas atmosphere, for example, in a nitrogen gas atmosphere. In the raw material blending step, for the purpose of suppressing the thermal oxidative decomposition of the polyamide resin or as a polycondensation catalyst, an addition of an alkali metal compound or a phosphorus compound or an addition of an aqueous solution for the purpose of adjusting a salt concentration can be performed.

[0026]

The dicarboxylic acid and the diamine which have been melt/stored in respective melting/storing tanks are quantitatively supplied from the respective melting/storing tanks to the next step, namely, the amidation step by respective raw material supply pumps. The term "supply accuracy C/A" at the time of supplying the dicarboxylic acid and the diamine from the raw material blending step to the amidation step denotes that at this time. The raw material supply pump is not particularly limited and it is preferable to use a plunger pump therefor.

[0027]

The amidation step is a step for subjecting the dicarboxylic acid and the diamine which are continuously supplied from the raw material blending step to a polycondensation reaction, to thereby convert them into a low polymer. As for an apparatus for performing the amidation step, a reactor of, for example, a pipe reactor method, a static mixer method or a continuous vertical type stirring tank method can be used. According to the invention, it is preferable to use the reactor of the pipe reactor method which does not require a liquid face control, is excellent in pressure resistance and low in an apparatus cost.

[0028]

When the reactor of the pipe reactor method is used, the dicarboxylic acid and the diamine supplied from the raw material blending step are subjected to the polycondensation reaction in the pipe reactor, to thereby form the low polymer. Control of the polymerization degree of the low polymer can be performed by adjusting a temperature and a pressure inside the apparatus and a retention period of time in such pipe. The retention period of time in the pipe can be adjusted by varying a pipe diameter, pipe length of the pipe reactor or a supply amount of the raw material. Reaction conditions inside



the reactor of the pipe reactor method vary depending on a structure or a polymerization degree of a desired polyamide resin but the temperature inside the apparatus is preferably from 110 to 300°C, more preferably from 120 to 290°C and, particularly preferably, from 130 to 280°C while the pressure inside the apparatus is preferably 1.2 MPa or less, more preferably 1.0 MPa or less and, particularly preferably, 0.9 MPa and the retention period of time is preferably from 5 to 120 minutes, more preferably from 10 to 110 minutes and, particularly preferably, from 15 to 100 minutes. When each of the above-described reaction conditions comes out of the above-described range, the polymerization degree of the low polymer is likely to be decreased, thermal degradation or cost increase in the apparatus is likely to be generated.

[0029]

The initial polymerization step is a step for enhancing a polymerization degree of the low polymer by evaporating condensed water in the low polymer continuously supplied from the amidation step or water used in adjusting a salt concentration. As for apparatuses for performing the initial polymerization step, a vertical stirring tank, centrifugal thin film type evaporator or the like can be used and, according to the

invention, the vertical stirring tank which can easily control the reaction conditions is preferred.

[0030]

When the vertical stirring tank is used, the polymerization degree of the polymer to be produced can be controlled by varying the temperature and pressure inside the apparatus and the retention period of time inside the apparatus. Favorable reaction conditions in the vertical stirring tank are as follows:

a temperature inside the apparatus is preferably from a melting point of the polymer to be produced to the melting point plus 40°C, more preferably from the melting point to the melting point plus 35°C and, particularly preferably, from the melting point to the melting point plus 30°C;

a pressure inside the apparatus is preferably 1.2 MPa or less, more preferably 1.0 MPa or less and, particularly preferably, 0.9 MPa; and

a retention period of time inside the apparatus is preferably from 10 to 150 minutes, more preferably from 15 to 140 minutes and, particularly preferably, from 20 to 130 minutes. When the above-described reaction conditions come out of respective ranges, the polymerization degree of the polymer to be produced tends to be decreased, or

thermal degradation or a deterioration of productivity comes to likely occur.

[0031]

In the above-described late polymerization step, the polymer supplied via the amidation step and the initial polymerization step is adjusted such that it has a desired polymerization degree. As for apparatuses for performing the late polymerization step, a twin-screw extruder, a single-screw extruder, a self cleaning reactor and the like can be used and, according to the invention, the twin-screw extruder which is excellent in kneading performance and easy in controlling the reaction is preferred.

[0032]

Then the twin-screw extruder is used, the polymerization degree of the polyamide resin to be produced can be controlled by varying a resin temperature, a vent vacuum degree, a screw rotation number and the retention period of time. The reaction conditions in the late polymerization step can appropriately be set in accordance with a structure or polymerization degree of a desired polyamide resin, a ratio of the carboxylic end group concentration to the amino end group concentration (CEG/AEG) and the like and favorable reaction conditions in the twin-screw extruder are as follows:

a resin temperature is preferably from a melting point of the amide resin to the melting point plus 50°C and, more preferably, from the melting point to the melting point plus 45°C;

a vent vacuum degree is preferably from 1 to 750 hPa and, more preferably, from 1 to 700 hPa; and

a retention period of time is preferably from 1 to 30 minutes, more preferably from 1.5 to 25 minutes and, particularly preferably, from 2 to 20 minutes. When the above-described reaction conditions come out of respective ranges, the polymerization degree of the polyamide resin tends to be decreased, or a thermal degradation, a deterioration of productivity or increase of a tertiary nitrogen comes to likely occur.

[0044]

[EXAMPLE]

#### EXAMPLE 1

In continuous production steps for polyamides containing a raw material blending step, an amidation step, an initial polymerization step and a late polymerization step, sodium acetate and sodium hypophosphite were dissolved in adipic acid (AA) which had been melted at 170°C in the melting/storing tank in the raw material

blending step such that sodium acetate became 0.102% by weight and sodium hypophosphite became 0.212% by weight. The resultant solution and m-xylylene which had been heated at 60°C in the melting/storing tank in the raw material blending step were continuously supplied to a pipe reactor (inner diameter: 20A; length: 13.5 m) in the amidation step by using respective plunger pumps at supply rates of 3.048 kg/hr and 2.828 kg/hr, respectively. In the amidation step, raw materials supplied in the pipe reactor were subjected to an amidation reaction by allowing them to be retained for about 35 minutes under conditions in that a pressure inside the apparatus was 0.15 MPa and a temperature inside the apparatus was elevated from 170°C to 245°C, to thereby obtain a low polymer having a polymerization degree of 1.45 in terms of Rv. The thus-obtained low polymer was continuously supplied to a vertical stirring tank equipped with an evaporation tube for evaporating condensed water generated by a stirring blade and a reaction. In the initial polymerization step, the low polymer was allowed to be retained in about 50 minutes under conditions: the temperature inside the apparatus was 265°C and the pressure inside the apparatus was 0.15 MPa, to thereby allow the low polymer to have a higher polymerization degree. The polymerization degree of the polymer which

came to have a higher polymerization degree was 1.85 in terms of  $R_v$ . The polymer was supplied to the twin-screw extruder (trade name: TEM-37BS; manufactured by Toshiba Machine Co., Ltd.) in the late polymerization step by using a gear pump at a supply amount of 8 kg/hr. In the late polymerization step, after the polymer was retained for about 5 minutes under the conditions that a resin temperature was 265°C, a vent vacuum degree was 500 hPa and a screw rotation number was 150 rpm, it was ejected in water and the thus-ejected polymer was cut by a cutter, to thereby obtain the polyamide resin. The retention period of time (a period of time required from a start of supplying the raw material to the amidation step to ejection of the polymer into water) was 90 minutes.